OUTLINE OF PROPOSED RESEARCH WORK

1. Name of Scholar:- - **VINOD KUMAR MEHTA**

2. Title of the Research Work:-

(In English) - **A study of Photocatalytic Degradation of some Commercially Important Dyes in presence of Modified Heterogeneous Catalyst**.

(In Hindi) - **˝okf.kfT;d jatdks dk ifj"d`r fo"kekaxh mRizsjdks dh mifLFkfr esa izdk'k mRizsjdh; fo?kVu˝**

3. Location:-

a) Institution /Department where the work is to be done - Department of Chemistry.
M. L. V. Govt. College.
Bhilwara (Rajasthan).

b) Geographical area of investigation (If any) - Not Applicable

(4) Introduction Importance of proposed investigation, Objectives:

Wastewaters from textile and dye industries are highly colored with large concentrations of organic matter. Direct discharge of textile industry wastewater into the receiving media causes serious environmental pollution by imparting intensive color and toxicity to aquatic environment. The azo dyes, are the largest class of dyes used in textile industry. Azo dyes have different forms, such as direct, acid, base, reactive, disperse, metal-complex, mordant and sulfur dyes. Almost one third of the dye use by textile industries as Azo dye. It is estimated that a remarkable amount of these dyes remains unfixed fabrics or fiber and is disposed to the effluent.

A lot of dyes having nitrogen and sulphur atoms which are environmentally and biochemically important are responsible for photo toxic and photo allergic behavior. In the environment, these compounds might be present in the effluent of industries which pollute the natural water as well as air. In this context, photo catalytic and chemical degradation processes have attracted the attention of photo chemists all over the world as these reactions have proved their importance in waste water treatment, bleaching of different classes of dyes, synthesis of organic compounds and other related activities. Most of the dyes are toxic and may be carcinogenic in nature.

The increasing world population with growing industrial products demands has led to a situation where protection of the environment has become a major issue and a crucial factor for several industrial processes, which will have to meet the requirements of the sustainable development of modern society. In order to combine industrial activities with preservation of the environment (sustainable development), there is a tendency in most countries to adopt rigid environmental legislation where the well-known Green Technology plays a key role.

Textile effluents are complex mixture containing a wide variety of dyes, natural impurities extracted from the fibers and other products such as dispersants, leveling agents, acids, alkalies, salts and sometimes heavy metals. In general the effluent is

highly colored with high biological oxygen demand (BOD) and chemical oxygen demand (COD). The effluent is discharged directly into water resources by the industries thus making the water unfit for all purposes.

Currently, the major methods of textile wastewater treatment involve physical and/or chemical processes such as membrane filtration, coagulation/flocculation, precipitation, flotation, adsorption, ion exchange, ion pair extraction, ultrasonic mineralization, electrolysis, chemical reduction and advanced chemical oxidation[1]. The advanced oxidation processes include, Fenton oxidation, photo catalytic oxidation UV/O_3, UV/H_2O_2, Sonification, photocatalysis, cavitation, e-beam irradiation, and wet-air oxidation.

The principle of green chemistry focus on reducing, recycling or eliminating the use of toxic chemicals by finding alternate ways to minimize the human and environmental impact without stifling scientific process. Therefore to overcome such problems, many researches are still needed in this direction. Hence the theme of the work is to offer a view for photo initiated reaction of nitrogen containing dyes in presence of modified heterogeneous catalyst such as $InMnO_3$, $SrTiO_3$, $MnWO_4$, $CeFeO_3$, $LaCrO_3$ and others.

Hence photo oxidation and photo bleaching of various nitrogen containing dyes may be regarded as model system for the study of mechanistic path for degradation including photolysis or sensitized photo oxidation by modified heterogeneous catalyst in presence of sun light.

Objective:-

The effluent of dyeing, printing, and textile industries pollutes water. Most of the dyes are toxic and carcinogenic in nature and make water colored and unfit for cleaning and irrigation purpose. The improper handling of these toxic chemicals has serious impact on the natural water bodies, land in the surrounding area, health and safety of workers. The contact with chemicals produces skin diseases like chemical burns, irritation, ulcers,

respiratory problem and may also be carcinogenic due to photodynamic change. The bleached dye solution is non-toxic (or less toxic) and hence less harmful.

There is little information about utilization of modified heterogeneous catalyst. in treatment of industrial effluent, exhaust purification etc.It can be effectively used for minimizing environment pollution. The modified heterogeneous catalyst. process may be applied to waste waters or contaminated soils, with following significance:-

1. Organic pollutant destruction.
2. Toxicity reduction.
3. Bio-degradability improvement.
4. Odour and colour removal.

Therefore, it is the main objective of present investigation to observe photo bleaching of some nitrogen containing dyes in presence of modified heterogeneous catalyst..
The objective of the present work may be summarized in following points.
1) Use of modified heterogeneous catalyst for the photo bleaching of nitrogen containing dyes.
2) Extent of bleaching in case of each dye will be studied in detail using spectrophotometric studies, chemical analysis, COD measurement etc.
3) A viable route for photo bleaching of the dye by will be chalked out. A tentative mechanism for the photochemical oxidation using modified heterogeneous catalyst reagent will be proposed.

(5) Review (work already done on the subject of proposed research study):

A solar photocatalytic degradation of the azo-dye acid orange 24 was carried out by means of a photo-Fenton reaction promoted by solar energy. The dye degradation was monitored during the experimental runs through UV/Vis absorption as well as COD and TOC concentration determination and toxicity reduction. In most cases, a discoloration higher than 85% was reached using 50 kJ/l of accumulated energy[1].

Carbofuran, one of the most toxic and biorefractory carbamate compounds, is widely used as insecticides. In the present study, a central composite design experiment was used to study the effect of modified heterogeneous catalyst. Treatment on carbofuran solution and to optimize the process variables such as carbofuran concentration (1–100 mg L^{-1})[2].

UV light induced degradation of textile dye, reactive red M5B has been carried out on TiO_2 and ZnO semiconductor particles. Spectrophotometer and COD techniques have been used to elucidate the details of dye decolourisation and degradation. The experiments have been carried out with different amount of catalyst, various concentration of dye solution, different irradiation time and in the presence of air. The reactive red M5B has been degraded to colourless end products. The results suggest that the photocatalytic degradation of textile dye may be a viable method for the safe disposal of wastewater[3].

Photooxidation of 4-nitrophenol (4-NP) in water by the UV/H_2O_2 advanced oxidation process was carried out in order to investigate the kinetics and pathway of 4-NP degradation. The experimental results showed that the photodegradation of 4-NP accorded well with pseudo-first order kinetics [4].

The effects of different parameters, such as H_2O_2 dosage, pH value and various anion scavengers on the degradation of 4-NP have been investigated in detail. It was found that acidic conditions are more favorable to the degradation of 4-NP but many anions, such as Carbonate,nitrate,and chloride slow down the photooxidation rate of 4-NP. Hydroquinone, 1,2,4-trihdroxybenzene, 4-nitropyrogallol, and 4-nitrocatechol were tentatively identified as the intermediates of 4-NP degradation by GC/MS after samples were derivatized by N,Obis (trimethylsilyl) - trifluoroacetamide (BSTFA)[5].

The decolorization of Reactive Yellow 86 (RY 86), one of reactive azo dyes, was investigated in the presence of Fenton reagent under solar light irradiation. The decolorization rate was strongly influenced by pH, initial concentrations of H_2O_2 and Fe(II), and so on .

Methodologies and emerging technologies on decolourization of industrial effluents. Optimization of Fenton's oxidation of chemical laboratory wastewaters using the response surface methodology was done by C. T. Benatti et al [6] and it was found that maximal COD removal (92.3%) was achieved when wastewater samples were treated at pH 4 in the presence of hydrogen peroxide and iron in the ratios
[COD] : $[H_2O_2]$ = 1:9 and $[H_2O_2]$: $[Fe^{2+}]$ = 4.5: 1

M. M. Alnuaimi et al[7] studied comparative decolourization of Neutral Red by different oxidative process namely the photo-oxidative process and the Fenton process. The dye was found to undergo substantial and rapid decoloration by both the methods. Conditions were optimized in both the sets of experiments to achieve the most efficient dye decolorations and Fenton approach was found to be more effective in photo bleaching of dyes.

An enhanced heterogeneous ferrioxalate photo degradation of reactive Orange-4 by solar light was reported and combined photo catalytic degradation and decolourization was studied[8]. Accelerated bleaching, photo bleaching and mineralization of non-biodegradable azo dye Orange-II was observed with oxone in solution with Co^{+2} ions in Fenton's like process by J. Fernandez et al[9]. The bleaching was found to be first order with respect to $[Co^{+2}]$ with rate constant 20 $M^{-1}S^{-1}$. The degradation of Acid Red 88 azo dye in water was investigated in lab scale experiments using a number of oxidation process and photo Fenton's ozone process ($O_3/H_2O_2/UV/Fe^{+3}$) seems to be more appropriate than O_3/TiO_2[10].

Degradation of azo dyes Azobenzene, p-Methyl Red and Methyl Orange in aqueous solution at room temperature has been studied by an advanced electrochemical oxidation process (AEOP) in presence of Fenton's reagent[11] and a pathway of degradation of azo dyes has been proposed.

Oxidative decomposition of Acid Brown 159 in aqueous solution by H2O2/Fe^{+2} and ozone was studied by W. K. Jozwiak et al[12] and full 100% decolourization is attained. Fenton reagent appeared to be more effective in comparison with ozonation.

Decolorization of aqueous solutions of Indigo carmine dye in an acid medium by H_2O_2/UV advanced oxidation process was studied[13]. The results shows that highly colored aqueous solutions of indigo carmine (9×10^{-5} M) can be effectively decolorized in an acid medium, in a short time interval (10 min) at room temperature and low H_2O_2 concentration (10^{-3} M). The effluent after treatment was colorless and nontoxic. Thus, H_2O_2/UV advanced oxidation process of indigo carmine may be an efficient alternative treatment for decolorizing textile wastewater containing this dye, in the referred experimental range of conditions.

Fenton-generated hydroxyl radicals removes the color of the Malachite Green (a basic dye with triphenylmethane group) almost (~98%) completely in weakly acidic aqueous medium. It was carried out by oxidative degradation pathways as evidenced from a remarkable lowering in the COD value of the product mixture in comparison to the title dye under identical conditions [14].

S.E.Lowum et al[15] carried out dye sensitized photo oxidation of Mushroom Tyrosinase. It was found that Fenton (H_2O_2/Fe^{+2}) and photo Fenton ($UV/H_2O_2/Fe^{+2}$) methods have proved to be effective and economical AOP methods used for the detoxification and degradation of many organic compounds and pesticides. The induced degradation of pesticides Amitrole (3-Amino-1,2,4-triazole) by excitation of iron(III)aqua complexes was investigated under irradiation at 365 nm[16].Photo-oxidation of some nitrogen containing explosives (DNT, TNT, RDX etc) was investigated by Fenton and Photo-Fenton process[-16-17].

The degradation of 2, 4, dinitro-toluene by Fenton reagent in water acetone mixture and investigated acetone reduced DNT degradation kinetics. a series of photo Fenton reactions for the degradation of TNT in reactor and reaction rate followed a pseudo-first order behavior and oxidation rate increases on increasing intensity of UV light,

concentration of ferrous ions and hydrogen peroxide.Reaction kinetics for the degradation of phenol and chlorinated phenol by Fenton reagent was studied by A. K. De[23]. On the basis of experimental observations, a probable mechanism for Fenton's degradation kinetics has been proposed. A rate equation was developed. Reaction rate constants for the degradation of three compounds i.e. phenol and *o*- and *p*-chlorophenols in Fenton reaction were calculated to have values of 2.53×10^7, 2.38×10^7, and 2.45×10^7 m^3 mol^{-1} s^{-1}, respectively [18-21.]

The degradation of 2-chloropyridine in synthetic aqueous solutions by means of ultraviolet and ultrasound irradiation has been investigated by D.R. Stapleton et al[24]. Light irradiation was generally more effective than ultrasound-driven degradation and complete substrate removal could be achieved in relatively short treatment times. On the other hand, ultrasound efficiency could be improved by coupling cavitations with the modified heterogeneous catalyst and selecting optimal reaction temperatures.

(6) Research Gaps identified in the proposed field of investigation. (Based on the review) :

Surat, Bhilwara, Pali, Balotra are well known industrial town having textile dyeing and processing industries. About 20 process house are there in Bhilwara in surrounding. Out of which 10 are situated on Hamirgarh road (on the banks of river Banas), 3 are situated on Pur road and 3 are on Ajmer road (on the banks of river Kothari). Approximately 20-21 lakh meter fabric is dyed in each process house per month as per its capacity and 2-2.5 metric ton dyes is used. It is expected that 15-18% of these are passed to effluent which is discharged in rivers or other water bodies. As these dyes are very toxic, it is necessary to photo bleach these dyes. Negligible attention has been carried out in the photo oxidation of nitrogen containing dyes by Photo Fenton process. Therefore it is planned to investigate the photocatalytic bleaching of these dyes of industrial importance by modified heterogeneous catalyst..

From the literature survey, it has been observed that oxidation and photo bleaching of toxic dyes by various traditional oxidizing agents like $KMnO_4$, Dichromate, Peroxydisulphate, MnO_2, enzymes has received considerable attention.

Along with it, the disintegration of organic pollutants present in textile waste water is carried out by number of methods like adsorption methods and microbial oxidation.

But an economical and technical solution has not yet been found for the treatment of aqueous effluent having recalcitrant compounds. Recent progress employs chemical, photochemical, sonochemical or radiolytic techniques which are advanced oxidation processes (AOP) to bring about chemical degradation modified heterogeneous catalyst. methods have proved to be effective and economical methods used for the detoxification and degradation of many compounds.

Main advantages of modified heterogeneous catalyst are as follows-

1. In context to cost effectiveness, it is one of the cheapest oxidizers that can be used.
2. Oxidation is based on generation of hydroxyl radicals that is considered as advanced oxidation processes (AOP).
3. Traditional oxidizing agents are not capable of breaking a number of organic compounds / dyes present in minute quantity or traces but Fenton reagent is capable of doing the same.
4. It has a high oxidation potential.
5. It is water soluble and easy to handle.
6. It exhibits a number of features that make its use advantageous as compared to conventional chemical and other methods, such as high degree of catalytic efficiency, high degree of specificity and absence of side reactions.
7. It can be easily removed from contaminant streams, easily standardized in commercial preparations and generally operate at mild conditions of temperature, pressure and pH.
8. Some oxidizing agents produce reduced products which are themself very toxic but by-products of Fenton reagent are non toxic (or very less toxic). Therefore it is planned to investigate the photo catalytic bleaching of these dyes of industrial importance by modified heterogeneous catalyst.

(7) Major Hypothesis:-

Modified heterogeneous catalysts such as $InMnO_3$, $SrTiO_3$, $MnWO_4$, $CeFeO_3$, $LaCrO_3$ and others has strong oxidizing ability as these can decolorize a wide range of dyes and in comparison to other oxidizing agents like titanium oxide , uranyl acetate etc, the process is relatively cheap and results generally in larger COD reduction. These characters provide substantial process energy savings and reduced manufacturing cost.

The heterogeneous photocatalysis has emerged as promising oxidatiove technique for degradation of detrimental organic compounds. The oxidation is based on the generation of hydroxyl radicals, hence it is considered as advanced oxidation process. Hydroxyl radicals are extraordinarily reactive and unstable species that attack most of the organic pollutant.

Heterogeneous photocatalysis is an attractive oxidative system since it does not require sophisticated instrumentation and expensive reagent. It has proven to be effective for complete mineralization of dyes or for their conversion into less toxic simple compounds that are more easily biodegradable. It is easy, economic and eco-friendly method for treatment of coloured waste water.

Hence photo oxidation and photo bleaching of various nitrogen containing dyes may be regarded as model system for the study of mechanistic path for degradation including photolysis or sensitized photo oxidation by modified heterogeneous catalyst in presence of sun light.

(8) Research Methodology:-

a. Selection of substrate:

Biological and industrially important Dyes (Reactive&Acidic) will be taken as substrate.

b. Selection of photo catalyst:

Modified heterogeneous catalyst ($InMnO_3$, $SrTiO_3$, $MnWO_4$, $CeFeO_3$, $LaCrO_3$ and other.in presence of light (Tungsten Lamp2×200W) will be used as photo catalyst.

c. Instruments required

- Light source (Visible and UV)
- Water jacket
- Aerator.
- Analytical balance.
- FTIR Spectrophotometer.
- UV-Vis Spectrophotometer
- Thin layer chromatography (TLC) kit.
- Centrifugal machine.
- Melting point apparatus.
- pH meter.
- Elemental analyzer.
- Glasswares as required.

d. Preparation of stock solution and reaction mixture:-

- The solutions of substrate (dye) will be prepared in the suitable solvent like methanol or water will be used after double distillation.
- Modified heterogeneous catalyst ($CeFeO_3$)
- Reaction Mixture-
  - The appropriate amount of target substrate will be dissolved in suitable solvent like methanol or water.
  - Appropriate amount of reagent solutions Modified heterogeneous catalyst ($SrTiO_3$, $CeFeO_3$, etc.) will be added to the substrate solution to prepare the reaction mixture.
  - The total volume of the reaction mixture will be made suitable by adding solvent.

e. Exposure to light and purging of air:-

- The reaction mixture will be exposed to light source (Visibal - Tungsten lamps; 2X200W and UV lamps).
- The distance between the light source and reaction mixture will be kept 30 cm. A water filter will be placed between the light source and reaction mixture to avoid thermal reaction.
- Air will be continuously purged through the reaction mixture with the help of an aerator which will continuously stir the reaction mixture and supply oxygen also.

f. Progress of the reaction:-

The progress of the reaction will be observed at definite time intervals by:

- ❖ UV-Vis Spectrophotometer (by measuring absorbance).
- ❖ Thin layer chromatography (TLC).

g. Control experiments:

The control experiments will also be performed to ascertain necessity of the ingredients.

1. Modified heterogeneous catalyst and oxygen (no exposure to light).
2. Light and oxygen (no catalyst will be added).
3. Catalyst and light (no oxygen will be bubbled).

h. Effect of reaction parameters:-

(1) Effect of concentration of substrate.

(2) Effect of amount of catalyst.

(3) Effect of hydrogen ion concentration.

(4) Effect of polarity of solvent.

i. Mechanism, Results and discussions:-

A tentative mechanism for photocatalytic reaction for each substrate

will be proposed followed by results and discussion.

j. Expected duration of the work (Year wise plan)

First year- Study of photo bleaching of 4-6 direct and acid dyes having azo group.

Second and third year - Study of photo bleaching of (2-4) reactive azo dyes, effluent water and compilation of data will be worked out.

k. Tentative chapter wise details of proposed Research:

The present work will be divided in three chapters.

CHAPTER-1

It will include detailed discussion of photochemistry, dyes and various photo catalytic reactions. An extensive literature survey related to the present work will also be discussed.

CHAPTER-2

It will include chemistry of modified heterogeneous catalyst including advance oxidation process will make part of discussion of chapter 2.

CHAPTER-3

It will include plan of work, detail of experimental set up, observation and inference along with product identification. A tentative mechanism for catalytic degradation for each dye will also be part of the chapter.

(9) List of References cited:

1. P. R .Gogate, A. B. Pandit: Advances in Environmental Research., 8(3- 4), (2004) 553.

2. J. J. Pignatallo, E. Oliveros, A. Mackay: Critical Reviews in Environmental Science and Technology., 36 (1), (2006) 1.

3. N. Bhatt, P. Sharma, R. Chandak and B. V. Kabra : Orient . J. Chem . Soc., 20(3), (2004) 609 .

4. M. M. Kondo, M. A. S. V. Arcos and M. T. Grassi: Braz. Arch. Biol. Technol., 45, (2002).

5. Y. Anjaneyulu, N . S. Chary. D. S. S. Raj: Environmental Science and Biotechnology., 4 (4) , (2005) 245.

6. C. T. Benatti , C . R. G. Tavares, T. A. Guedes : Journal of Environmental Management., 80 (1), (2006) 66.

7. M. M. Alnuaimi , M A. Rauf, S. S. Ashraf: Dyes and Pigments, 72 (3), (2007) 367.

8. K. Selvan , M . Muruganandham , M . Swaminathan : Solar energy materials and solar cells ., 89 (1) , (2005) 61.

9. J. Fernandez, P . Maruthamuthu , A . Renken , J . Kiwi: Applied Catalysis B: Environmental, 49 (3), (2004) 207.

10. J. R. Domiguez, J. Beltron , O. Rodriguez: Catalysis Today., 101 (3- 4), (2005) 389.

11. E. Guivarch, C. Lahitte, M. A. Oturan: Environmental Chemistry Letters., 1 (1), (2003) 38.

12. W. K. Jojwiak, M. Mitros R. Tosik: Dyes and Pigments, 74 (1) (2007) 9.

13. E. Rodriguez, R. Peche , J. M. Merino, L. M. Camarero: Environmental Engineering Science. , 24(3), (2006) 363.

14. K. Dutta, S. Bhattacharjee , B . Chaudhuri, S. Mukhopadhyay : J . Environmental Science & Health., 38 (7), (2003) 1311.

15. C. Catastini, S. Rafqah, G. Mailhot, M. Sarakha: J. Photochem. Photobiol A: Chem., 162 (1) ,(2004) 97.

16. M. J. Liou, M. C. Lu, L. N. Chen: Water Res., 37 (17), (2003) 3172.

17. S. Y. Oh, P. C. Chiu, B. J. Kim, D. K. Cha: Water Res., 37(17), (2003) 4275.

18. C. M. Miller, K. C. Bower, C. Ries; Environmental Engineering Science., 20(1), (2003) 65.

19. M. J. Liou, M. C. Lu, L. N. Chen; Chemosphere. , 57 (9), (2004) 1107.

20. A. K. De, B. K. Dutta, S. Bhattacharjee ; Environmental Progress., 25 (1), (2005) 64.

24. D. R. Stapleton, R. J. Emery. , C. Smith: International Journal of Environment and Pollution. 28(1-2), (2006) 87.

21. Legrini ON, Oliveres E and Braun AM, Photochemical processes for water treatment. Chem Rev 93:671–698 (2008).

22. Hoffmann MR, Martin ST and Won Yong Choi, Environmental application of semiconductor photocatalysis. Chem Rev. 95:69–96 (2009).

23. Pontius FW, Complying with the new drinking water quality regulations. J Am Water Works Assoc 82:2–52 (2010).

24. Lyseffe Plant and Martin Jeff, Hydrogen peroxide: a potent force to destroy organics in wastewater. Chem Engin 101:EE16–20 (2011).

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29.10.11

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